

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

EFFECT OF OZONATION ON RECYCLED FIBER PROPERTIES

Project 2697-53

Report One

A Progress Report

to

MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

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SUMMARY

Recent work indicates that ozonation of high yield pulp is one way to improve bonding. In view of its possible application to recycled fiber, work is in progress to determine if ozonation treatments are effective on old corrugated containers (OCC) and its component fibers. This work is being carried out under Institute funding.

After process improvements were made, a series of trials were carried out on OCC using treatment times varying from 5 to 90 minutes. Three replicate trials were made at each treatment time. Ozone consumption levels ranged from about 0.8% on oven-dry (o.d.) fiber at 5 minutes to about 12% at 90 minutes. The results are briefly summarized below.

1. At ozone consumption levels of about 2.3% or more, large increases were obtained in most handsheet properties which are highly dependent on fiber-to-fiber bonding. For example, at 2.3% O_3 consumption, burst and tensile increased about 35 and 27%, respectively. Much larger percentage increases were generally obtained as the O_3 consumption increased.
2. Modified ring compression increased with increasing O_3 consumption, at a slower rate than burst and tensile.
3. Tearing strength decreased with increasing O_3 consumption; the average loss was relatively small (-2.9%) at 2.3% O_3 consumption.

4. The freeness decreases at consumptions near 2.3% were small and possibly not significant. Thus, ozonation tends to produce significant changes in pulp properties without much effect on freeness.
5. Photomicrographs show that ozonation modifies the surface of the fiber and increases the conformability and, hence, bonding of the fiber when it is made into the sheet.
6. Preliminary cost estimates indicate that ozonation operating costs to achieve a 35% burst improvement would be about \$12.50 per ton of treated fiber without considering possible savings in refining. The latter savings might amount to \$3-4 per ton. Capital costs would be about \$4.50-\$5.00 per ton of treated fiber.
7. Thus, it appears that ozone treatments can significantly increase most strength properties of OCC without any major reduction in freeness. The process should present little or no pollution problem and should have no detrimental effect on the white water system.

INTRODUCTION

One approach to improving the bonding potentials of recycled fiber is to utilize chemical treatments which will mildly increase delignification, swelling, or fibrillation of the fibers. A number of such treatments are discussed in the research plan for this project. Recent work indicates that ozonation of high-yield pulp is a promising way to improve bonding. In view of its possible application to recycled fiber, work is in progress to determine if ozonation treatments are effective on old corrugated containers (OCC) and its component fibers. This work is being carried out under Institute funding.

LITERATURE REVIEW

A literature search was carried out on the ozone treatment of wood and/or pulp fiber with special reference to recycled fiber. The bulk of the published work covers ozone treatments of mechanical and chemimechanical pulps with only a limited amount of research on chemical pulps. Little or no work has been done on recycled fibers. Therefore, this abridged review primarily covers ozone treatments of "mechanical" pulps with particular reference to strength.

The reactions between ozone and the various chemical components in wood (especially lignin) have long been of interest to wood chemists. As early as 1912, Cunningham and Doree carried out experiments with ozone and found that it acted as a delignifying agent (1). They also found that although ozone had little effect on dry cellulose, it attacked cellulose in the wetted state. At this early date, it was observed that the presence of moisture played a key role in the reactivity between wood fiber and ozone. In more recent work, Osawa and Schuerch suggested that the immobilized water layer surrounding the fibers was the controlling factor (2). At 30-50% consistency, the fluid layer is apparently thin enough to have a minimal effect on the diffusion rate. It was found that the reaction between ozone and pulp was rather rapid in this consistency range. It was shown that below 30% consistency, the fluid layer increases and the reaction rate decreases rapidly. In brief, ozonation treatments appear to be most effective on well fluffed pulps in the 30-50% consistency range.

However, Lindholm (3) was able to achieve a reasonable degree of reactivity (ca. 80%) at low consistency using special equipment and methods. He noted that at low consistency the ozone tends to react with the fines, whereas in gas phase treatments, the ozone reacts more uniformly with the different fiber fractions. Thus, it appeared that tensile strength increased less in the

low consistency treatments than in gas phase treatments. For this reason he suggested that low consistency treatments may have advantages in treating the coarse fiber fraction of pulp. Low consistency treatments may be worth further investigation on OCC and both the long and short fiber fractions.

Although ozonation work on a laboratory scale has gone on since about 1912, serious process development did not start until the mid-1960's. The research was chiefly concerned with the bleaching of mechanical pulps with ozone alone or with other chemical treatments (2,4-13). In a series of papers, Soteland and coworkers from Norway (Norwegian Pulp and Paper Institute) reported on work they had done on the bleaching of mechanical, chemimechanical, and thermomechanical pulps with oxygen and ozone (9-11,14). As a part of this work using ozone as a bleaching agent, it was found that significant strength improvements (particularly in tensile strength) resulted from these treatments. Although the theories may differ to some extent, it was generally believed that this strength improvement was a result of the hydrophilization of the lignin and a modification of the fiber surface. This gave a more conformable, more bondable, and hydrophilic fiber (15). The main reaction may involve cleavage of isolated carbon-carbon double bonds whereby carbonyl and peroxide groups are formed. It was demonstrated that the ozonation of mechanical pulps introduces carboxylic acid groups in the pulp and that the determination of carboxyls served as an indicator of the treatment effectiveness and correlated with at least some of the physical properties (9,16).

The main attack by ozone is on the phenolic structures, explaining the increase in carbonyl groups and the reduction in the aromatic character of the lignin.

Soteland also concluded that mechanical refining was inferior to ozonation as a means for obtaining strength at suitable freeness levels on the "mechanical" pulps studied (17).

Proctor (18) carried out ozonation treatments on western hemlock kraft pulp. He observed that the development of strength properties (higher burst and tensile, lower tear) is somewhat similar to mechanical beating but without reduction in fiber length. The increases in bonding were attributed to the production of hemicellulose-like material. The development of strength properties on refining of ozonated pulp was reported to be similar to that of untreated pulps but the beating time to a given freeness was much shorter: Proctor employed a low O_3 to O_2 concentration (ca. 0.1%) as compared to other investigators — usually 2% or higher (3,11,19). While he felt that ozonation had no particular advantage over refining for his conditions, he cautioned that more favorable results could possibly be obtained with a larger ozone generator. He also found that the uniformity of consistency in the fluffed state could be important to treatment efficiency.

In 1975-76, a pilot operation was established in Norway at the Holmen Hellefos newsprint mill starting up in the summer of 1976. It was capable of treating about five tons per day of mechanical pulp. Limited production of a commercial newsprint was made with rather significant success. The object was to substitute ozonated thermomechanical and/or stone groundwood for all or part of the chemical furnish in the newsprint (17).

Pilot operations have also been set up at the Pulp and Paper Research Institute of Canada. The major effort has been the establishment of the Papri-zone bleaching process (11).

It has been rather well established that the optimum results are obtained by treating pulp with ozone in a gaseous phase at a consistency of 30-50%. No figures are readily available on production costs directly related to the treatment of pulp. It has also been established that the condition of the fiber to be treated is very important in order to obtain uniform treatment and maximum ozone consumption on the fibers.

EXPERIMENTAL PROCEDURES

DEWATERING AND FLUFFING

In the first series of ozonation trials (results not shown herein), the slushed OCC was dewatered on a Buchner funnel using a rubber sheet for compression of the damp pad. The damp pads were then broken up by hand and run through a pulp shredder before being placed in the ozonator. With this treatment, the pulp consistencies were about 25-30%, and the pulp was not particularly well fluffed. The ozone reaction efficiencies were only about 50%, and it appeared that the ozone was probably not reacting uniformly with the fibers due to the excessive "balling" of the fibers before and during treatment. Microscopic examination of fibers stained with C stain confirmed that nonuniform ozonation was the major problem.

The literature indicates that a more optimum treatment consistency would be in the neighborhood of 40%. However, if the increased consistency is produced by drying at room or elevated temperature, the fibrous mass is more difficult to fluff, and nonuniform moisture contents are obtained. Parts of the fibrous mass dry too much, which would be expected to reduce treatment uniformity and efficiency. Removal of water by pressing made the fiber mass more difficult to fluff.

It was found that a well fluffed OCC pulp at about 40-45% consistency could be obtained as follows:

1. Centrifugal dewatering to 25-30% consistency.
2. Fluffing and additional water removal to a consistency of 40-50% by repeatedly passing the dewatered pulp through a pulp shredder built at the Institute. This consists merely of a vertical rotating shaft with blunt horizontal bars protruding from the shaft.

The above procedure improved ozone reaction efficiencies significantly as discussed in later pages.

OZONATION

The ozonation was carried out on a Welsbach ozonator at room temperature (Fig. 1). The concentration of O_3 in the O_2 stream was about 2%. The gas stream from the ozonator was split into two parts in a ratio of 4:1. The smaller stream was passed into a double trap system containing potassium iodide to determine the ozone addition. The larger stream passed through a flask containing the pulp to be treated. The effluent gas from the flask was analyzed for residual ozone content, and the consumption was determined by difference.

Ozone concentrations were determined by absorption of ozone in potassium iodide solution, acidification, and titration of the liberated iodine with sodium thiosulfate solution to a starch end point. The pH of the pulp was determined before and after treatment and after washing the ozonated pulp in tap water.

HANDSHEET TESTING

Standard British handsheets were made from each pulp and the untreated fluffed control. Prior to handsheet preparation, the pulp was washed with tap water to raise the pH.

The following tests were performed.

	No. of Determinations per Condition
1. Basis weight	10
2. Caliper	10
3. Apparent density	
4. Burst	10
5. Elmendorf tear	4

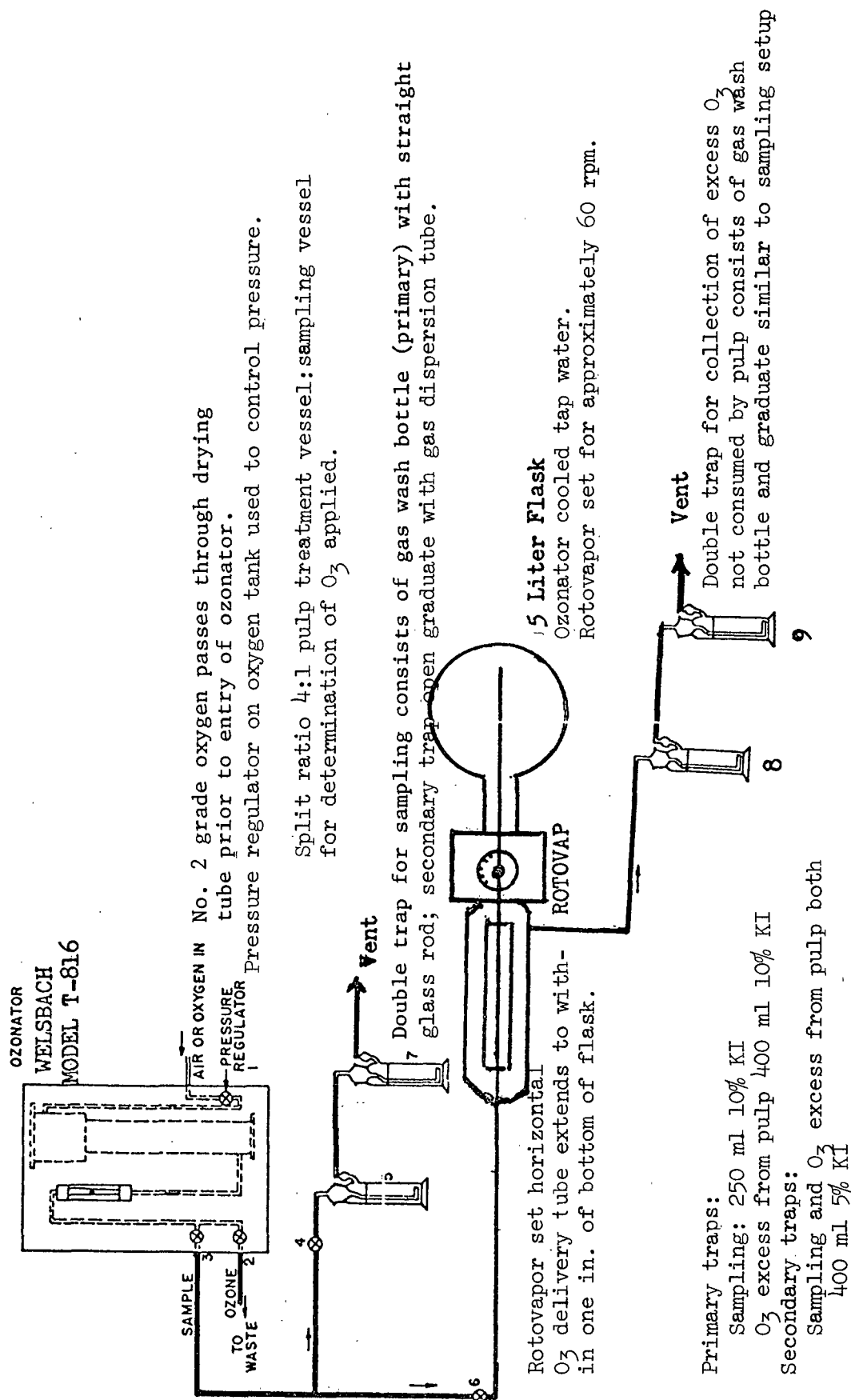


Figure 1. Ozonation Flow Diagram

	No. of Determinations per Condition
6. Modified ring compression	10
7. Tensile	10
8. Stretch	10
9. Tensile stiffness (Et)	10
10. Tensile energy absorption	10
11. Zero-span tensile	5
12. Brightness	6
13. ZDT strength	5

DISCUSSION

After developing the improved dewatering and fluffing procedures described previously, ozonation trials were carried out on the fluffed OCC using treatment times of 5, 10, 15, 60 and 90 minutes. At each time, three replicate batches were ozonated. Each batch was then made into handsheets, and the sheets from each batch were separately evaluated. Four batches of the fluffed untreated OCC were also made into sheets and evaluated to serve as control runs.

The ozone consumption and handsheet test results for each replicate batch are tabulated in Tables I and II, respectively. The average results obtained at each ozone treatment level are summarized in Table III.

The ozone consumption increased from 0.814% at 5 minutes to about 12% of o.d. fiber at 90 minutes (Fig. 2). The changes in O_3 consumption were approximately proportional to treatment time.

The ozone consumption results in Table I and Fig. 2 show that the treatment efficiencies (ozone consumption as percent of applied) achieved in these trials were in excess of 98% for treatment times up to 15 minutes. Even at 90 minutes, the treatment efficiency was greater than 80%. These treatment efficiencies are considerably higher than achieved in the first trials on OCC (47-64%). The better treatment efficiencies obtained in these trials are believed to be due to the more uniform dewatering and improved fluffing of the pulp prior to ozone treatment.

MICROSCOPIC EXAMINATION OF TREATED FIBERS AND SHEETS

Optical and scanning electron microscope (SEM) studies were carried out to characterize the effects of ozonation on the physical appearance of fibers.

TABLE I
OZONE PROCESSING RESULTS

Trial	Ozone Treatment Interval, min	Ozone Applied, %	Ozone Consumed, %	Ozone Reaction Efficiency, %	Canadian Standard Freeness, cc
1	0	0.000	0.000	0.0	650
2	0	0.000	0.000	0.0	650
3	0	0.000	0.000	0.0	660
4	0	0.000	0.000	0.0	570
Av.	0	0.000	0.000	0.0	633
1	5	0.838	0.832	99.2	650
2	5	0.806	0.800	99.2	640
3	5	0.816	0.809	99.2	650
Av.	5	0.820	0.814	99.2	647
1	10	1.59	1.57	98.7	600
2	10	1.56	1.54	98.7	640
3	10	1.68	1.65	98.0	640
Av.	10	1.61	1.59	98.5	627
1	15	2.35	2.32	98.6	630
2	15	2.30	2.25	97.9	600
3	15	2.39	2.35	98.3	620
Av.	15	2.35	2.31	98.3	617
1	60	9.33	8.51	91.3	540
2	60	9.36	8.50	90.8	550
3	60	9.53	8.57	89.9	610
Av.	60	9.41	8.53	90.7	567
1	90	13.95	11.83	84.8	590
2	90	14.61	12.01	82.2	560
3	90	14.86	12.37	83.2	560
Av.	90	14.47	12.07	83.4	570

TABLE II
HANDSHEET RESULTS

Trial	Ozone Consumed, %	Basis Weight, lb/M ft ²	Caliper, mils	Apparent Density	Burst Factor	Mod. Ring Factor	Tear Factor	Tensile Factor	Stretch, %	Et Factor	TFA, ft-lb/ft ²	ZDT, lb/in ²	Zero Span Factor, km	Brightness, %
1	0.0	13.2	6.6	2.00	1.24	0.242	6.76	0.90	1.67	125.8	1.7	---	12.72	17.4
2	0.0	13.1	5.7	2.30	1.42	0.321	6.45	1.00	1.97	131.3	2.2	61.2	13.58	16.4
3	0.0	13.3	6.5	2.03	1.12	0.282	6.76	0.85	1.81	116.5	1.8	43.0	12.93	16.2
4	0.0	13.3	5.7	2.31	1.43	0.290	6.58	0.99	2.00	123.0	2.2	53.8	12.68	16.3
Av.	0.0	13.2	6.1	2.16	1.30	0.284	6.64	0.94	1.86	124.2	2.0	52.7	12.98	16.6
1	0.832	13.2	6.1	2.17	1.31	0.291	6.60	0.97	1.77	131.1	2.0	46.4	13.31	18.1
2	0.800	14.8	6.6	2.25	1.38	0.320	7.17	0.95	2.06	125.4	2.5	43.4	12.52	17.9
3	0.809	13.7	6.5	2.11	1.40	0.321	7.02	0.94	2.04	124.5	2.2	46.4	12.89	18.5
Av.	0.814	13.9	6.4	2.18	1.36	0.311	6.93	0.95	1.96	127.0	2.2	45.4	12.94	18.2
1	1.57	13.5	6.1	2.22	1.44	0.307	6.98	0.98	2.04	129.3	2.4	49.8	13.25	18.2
2	1.54	14.0	6.2	2.24	1.48	0.322	7.01	1.02	2.18	133.8	2.7	49.2	12.46	19.0
3	1.65	13.3	6.1	2.17	1.55	0.308	6.62	1.04	2.12	134.4	2.5	54.4	12.73	20.2
Av.	1.59	13.6	6.1	2.21	1.49	0.312	6.87	1.01	2.11	132.5	2.5	51.1	12.81	19.1
1	2.32	13.2	5.6	2.36	1.82	0.280	6.48	1.24	2.16	153.8	3.0	---	12.76	20.0
2	2.25	13.6	6.0	2.25	1.63	0.339	6.65	1.10	2.13	139.4	2.8	53.2	13.01	20.5
3	2.35	12.7	5.3	2.42	1.84	0.302	6.22	1.23	2.26	150.3	3.0	70.2	13.07	20.2
Av.	2.31	13.2	5.6	2.34	1.76	0.307	6.45	1.19	2.18	147.8	2.9	61.7	12.95	20.2
1	8.51	13.6	5.1	2.69	2.44	0.359	5.28	1.48	2.38	166.6	4.0	93.8	13.93	33.8
2	8.50	13.1	5.5	2.38	2.56	0.351	5.47	1.54	2.40	180.2	4.1	---	13.98	34.0
3	8.57	13.9	5.4	2.54	2.34	0.350	5.19	1.41	2.52	169.3	4.2	92.2	12.48	32.5
Av.	8.53	13.5	5.3	2.54	2.45	0.353	5.31	1.48	2.43	172.0	4.1	93.0	13.46	33.4
1	11.83	13.5	5.4	2.50	2.81	0.400	5.01	1.64	2.46	192.6	4.6	---	13.37	48.4
2	12.01	13.4	5.0	2.65	2.42	0.374	4.07	1.56	2.17	190.3	3.8	100.4	13.05	42.5
3	12.37	13.2	5.1	2.61	2.35	0.349	4.39	1.53	2.26	186.5	3.9	102.0	12.23	42.9
Av.	12.07	13.4	5.2	2.59	2.53	0.374	4.49	1.58	2.30	189.8	4.1	101.2	12.88	44.6

TABLE III
SUMMARY OF AVERAGE HANDSHEET PROPERTIES

Test ^a	Ozone Consumption, %					
	0	0.814	1.59	2.31	8.53	12.07
Ozonation time, min	0	5	10	15	60	90
C.S. freeness, cc	633	647	627	617	567	570
% change	--	+2.2	-0.9	-2.5	-10.4	-10.0
Basis weight, lb/M ft ²	13.2	13.9	13.6	13.2	13.5	13.4
Caliper, points	6.1	6.4	6.1	5.6	5.3	5.2
Apparent density	2.16	2.18	2.21	2.34	2.54	2.59
% change	--	+0.9	+2.3	+8.3	+17.6	+19.9
Bursting strength, psig	17.2	19.0	20.3	23.2	33.1	33.8
Factor	1.30	1.36	1.49	1.76	2.45	2.53
% change	--	+4.6	+14.6	+35.4	+88.5	+94.6
Mod. ring compression, lb/inch	3.8	4.3	4.2	4.0	4.8	5.0
Factor	0.284	0.311	0.312	0.307	0.353	0.374
% change	--	+9.5	+9.9	+8.1	+24.3	+31.7
Tear, g	87.6	96.7	93.5	85.1	71.9	60.0
Factor	6.64	6.93	6.87	6.45	5.31	4.49
% change	--	+4.4	+3.5	-2.9	-20.0	-32.4
Tensile, lb/inch	12.4	13.3	13.8	15.6	20.0	21.0
Factor	0.94	0.95	1.01	1.19	1.48	1.58
% change	--	+1.1	+7.4	+26.6	+57.4	+68.1
Stretch, %	1.86	1.96	2.11	2.18	2.43	2.30
% change	--	+5.4	+13.4	+17.2	+30.6	+23.7
Et, lb/inch	1640	1767	1802	1946	2326	2536
Factor	124.2	127.0	132.5	147.8	172.0	189.8
% change	--	2.3	+6.7	+19.0	+38.5	+52.8
TEA, ft-lb/ft ²	2.0	2.2	2.5	2.9	4.1	4.1
% change	--	+10.0	+25.0	+45.0	+105.0	+105.0
ZDT, psi	52.7	45.4	51.1	61.7	93.0	101.2
% change	--	-13.9	-3.0	+17.1	+76.5	+92.0
Brightness, %	16.6	18.2	19.1	20.2	33.4	44.6
% change	--	+9.6	+15.1	+21.7	+101.2	+168.7
Zero-span factor, km	12.98	12.94	12.81	12.95	13.46	12.88
% change	--	-0.3	-1.3	-0.2	+3.7	-0.8

^a Abbreviations: Et = tensile stiffness = product of Young's modulus times thickness; TEA = tensile energy absorption; ZDT = Z-direction tensile.

NOTE: Percent changes are based on untreated results as reference.

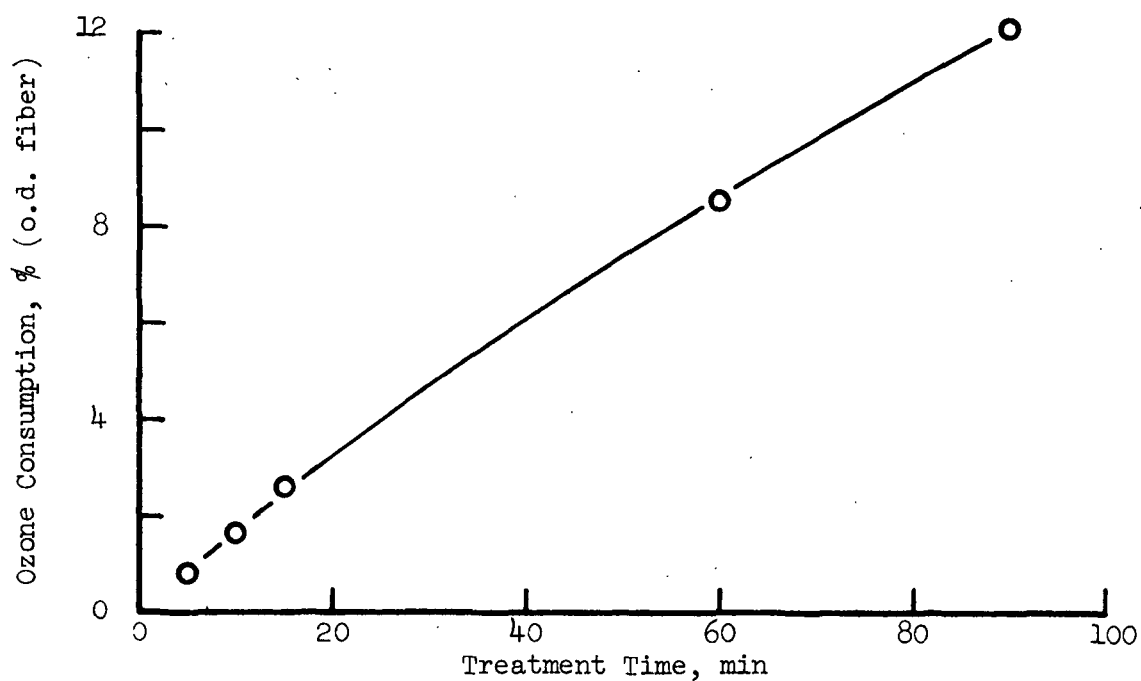
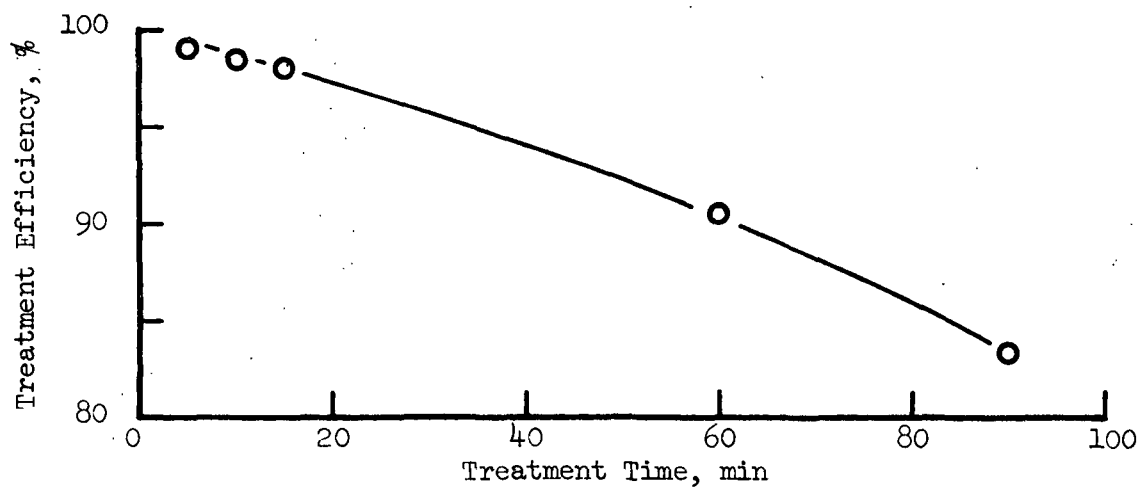


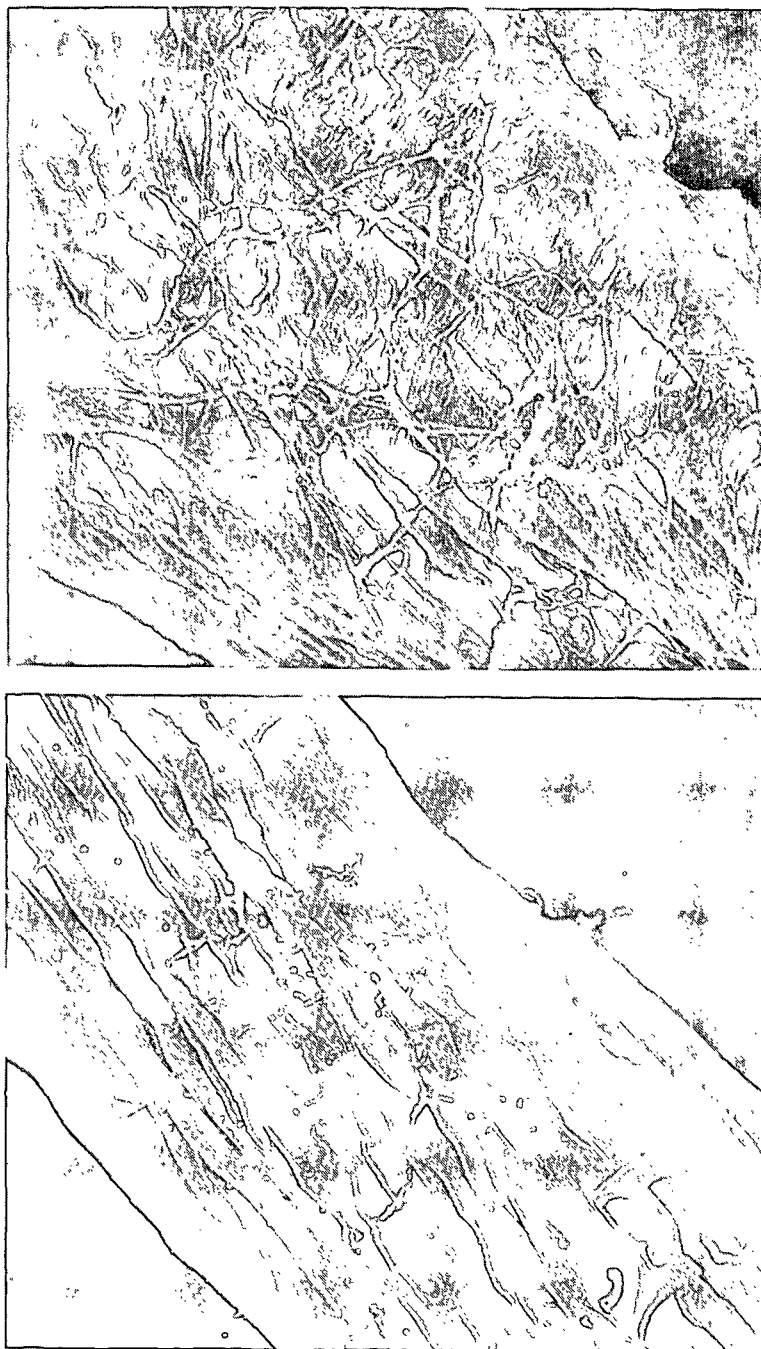
Figure 2. Ozone Consumption and Treatment Efficiency

Softwood unbleached kraft and hardwood unbleached NSSC which make up the composition of the OCC normally stain orange-yellow to yellow with the "C" stain reagent used in fiber analysis. It was found that as ozonation proceeds, the fiber color response with "C" stain shifts to blue. It was also observed that the different fiber cells respond to color changes at different rates. The softwood (earlywood) and hardwood vessel elements are first to show a response with "C" stain followed by the hardwood fibers and finally by the softwood summerwood (latewood). Table IV shows the degree of color change to blue with increasing ozone treatment in the opinion of the analyst. It is speculated that these differences in fiber behavior are related to fiber density, lignin modification (bleaching/delignification), and/or other differences in the chemical nature of the various fibrous elements present.

TABLE IV
"C" STAIN COLOR CHANGES WITH OZONATION

Ozone Consumed, % o.d. fiber	Estimated Percentages of Total Fiber Colored Blue			
	Softwood		Hardwood	
	Springwood	Summerwood	Vessels	Fibers
0.0	0	0	0	0
2.3	25	0	25	0
8.5	80-90	25-30	80-90	80-90
11.8	90	75	90	90

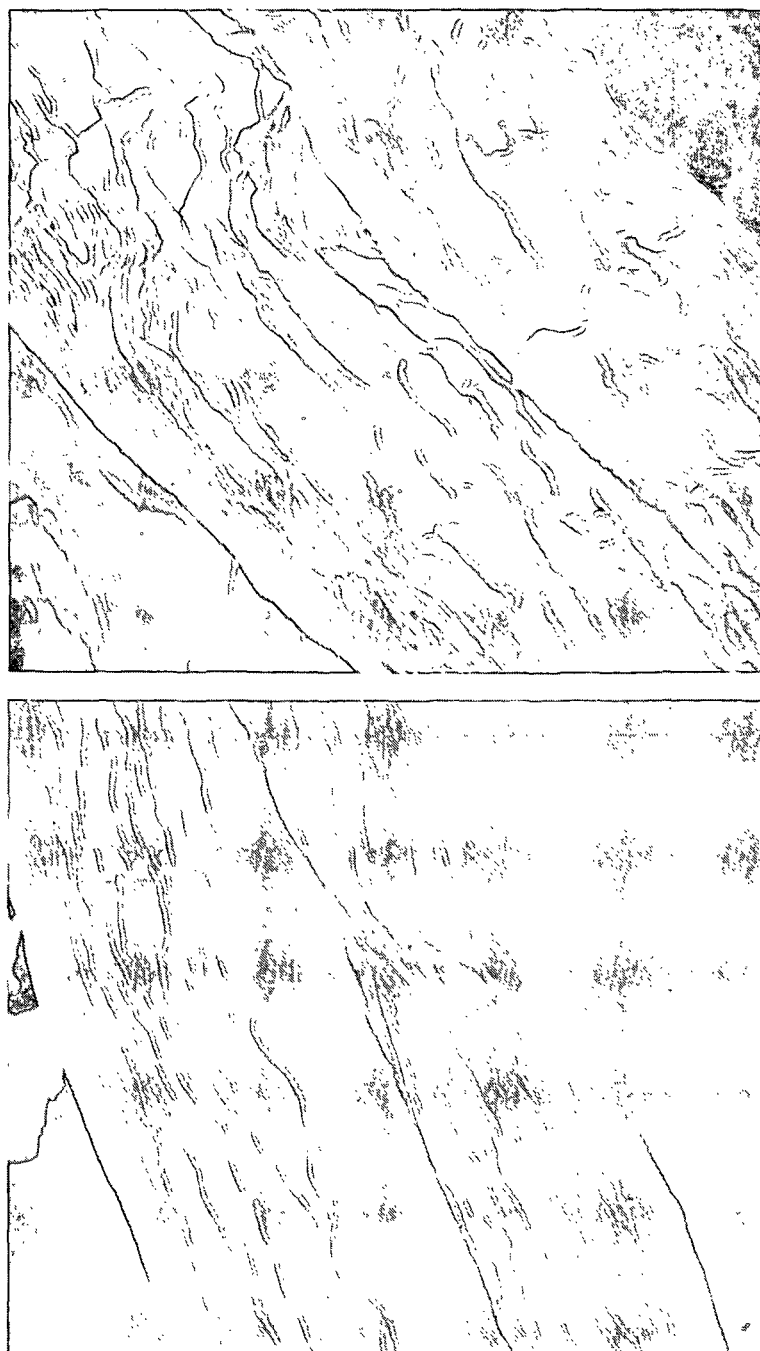
SEM studies of critical point and air-dried fibers were also carried out. Figures 3 and 4 show micrographs of fiber walls of untreated fibers and fibers treated with 11.8% ozone after critical point drying and air drying, respectively. Critical point dried fibers after ozonation show microfibril surface detail and other surface modifications not shown by the untreated fibers. The surface changes are most easily observed in the critical point dried fiber



Untreated

Ozonated - 11.8%

Figure 3. Critical Point Dried Fibers Before and After Ozonation (SEM - 3000X)



Untreated

Ozonated - 11.8%

Figure 4. Air-Dried Fibers Before and After Ozonation (SEM - 3000X)

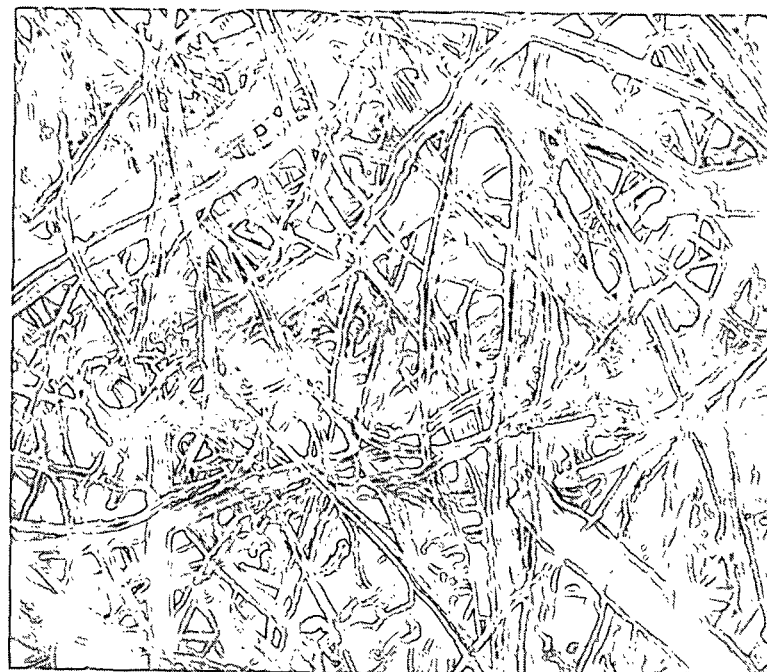
photographs (Fig. 3), but can also be observed in the shrinkage effects shown by the air-dried fibers (Fig. 4).

Scanning electron micrographs of the handsheets prepared for physical testing also show differences in mat conformability and potential fiber bonding between ozone treated and untreated fibers. The air exposed "rough" surfaces of the handsheets are illustrated in Fig. 5 and 6 at magnifications of 100 and 500X, respectively. The ozonated fibers appear to exhibit increased fiber-to-fiber contact and conformability as compared to the untreated fibers at both magnifications. Also, at 500X the ozonated fibers appear to conform sufficiently so that the detail contour of the immediate underlying fibers can be seen. Thus, the photographs suggest that ozonation provides fibers with not only increased microfibril surface but also reduced fiber rigidity. As a result, inter- and intrafiber bonding are enhanced in the formed sheet.

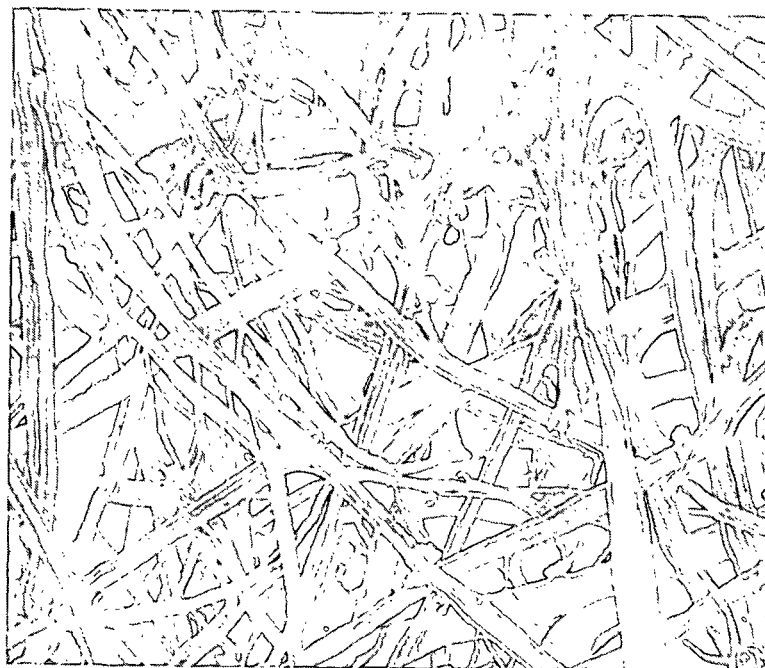
In brief, ozonated fibers appear more conformable, thus providing more and stronger bonded area. In this sense, the advantages of refining are apparently achieved without some of the disadvantages such as reduced freeness, increased fines, etc. The Bauer McNett fiber classification results in Table V show that ozonation had no significant effect on the distribution of fibers in the various screen fractions. Thus, as would be expected, ozonation did not increase the fines content. In addition, Table VI shows that ozonation did not change the proportions of softwood and hardwood fibers in the screen fractions.

PHYSICAL TEST RESULTS

The average changes in physical characteristics are shown in Fig. 7 and 8 for the various ozone treatment levels. In general, at ozone consumptions of 2.3% or more, substantial increases were obtained for those mechanical properties



Ozonated - 11.8%



Untreated

Figure 5. Handsheets from Ozonated and Untreated Fibers (SEM - 100X)



Ozonated — 11.8%



Untreated

Figure 6. Handsheets from Ozonated and Untreated Fibers (SEM — 500X)

TABLE V
BAUER-McNETT FIBER CLASSIFICATION RESULTS

Ozone Consumption	Fiber Retained on Indicated Screen, %				
	on 35	through 35 on 65	through 65 on 100	through 100 on 150	through 150 (by difference)
Untreated	62.2	17.0	3.7	2.1	15.0
2.35	59.8	17.7	4.2	2.0	16.3
8.57	57.3	15.6	3.7	1.4	22.0
12.01	62.6	16.0	3.7	2.2	15.5

TABLE VI
FIBER ANALYSIS OF BAUER-McNETT FIBER FRACTIONS

Ozone Consumed by Fiber, %	Retained on 35		Pass 35 Ret. 65		Pass 65 Ret. 100	
	Soft-wood	Hard-wood	Soft-wood	Hard-wood	Soft-wood	Hard-wood
Untreated	94	6	33	67	17	83
2.35	95	5	38	62	13	87
8.57	95	5	35	65	13	87
12.01	91	9	32	68	14	86

Ozone Consumed by Fiber, %	Pass 100 Ret. 150		Passed 150 Mesh	
	Soft-wood	Hard-wood	Soft-wood	Hard-wood
Untreated	13	87	--	--
2.35	15	85	--	--
8.57	12	88	--	--
12.01	13	87	--	--

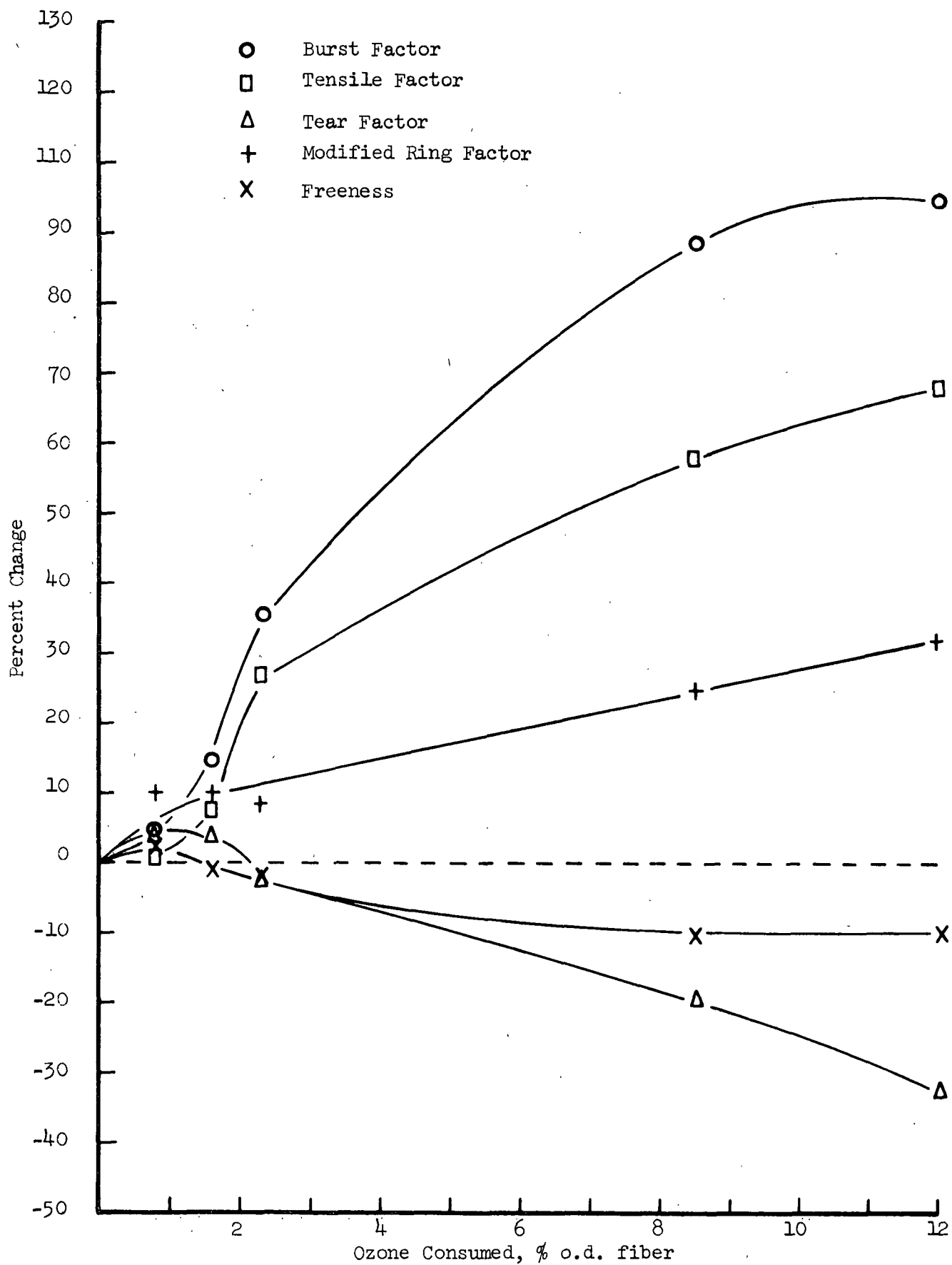


Figure 7. Effect of Ozonation on Handsheet Properties

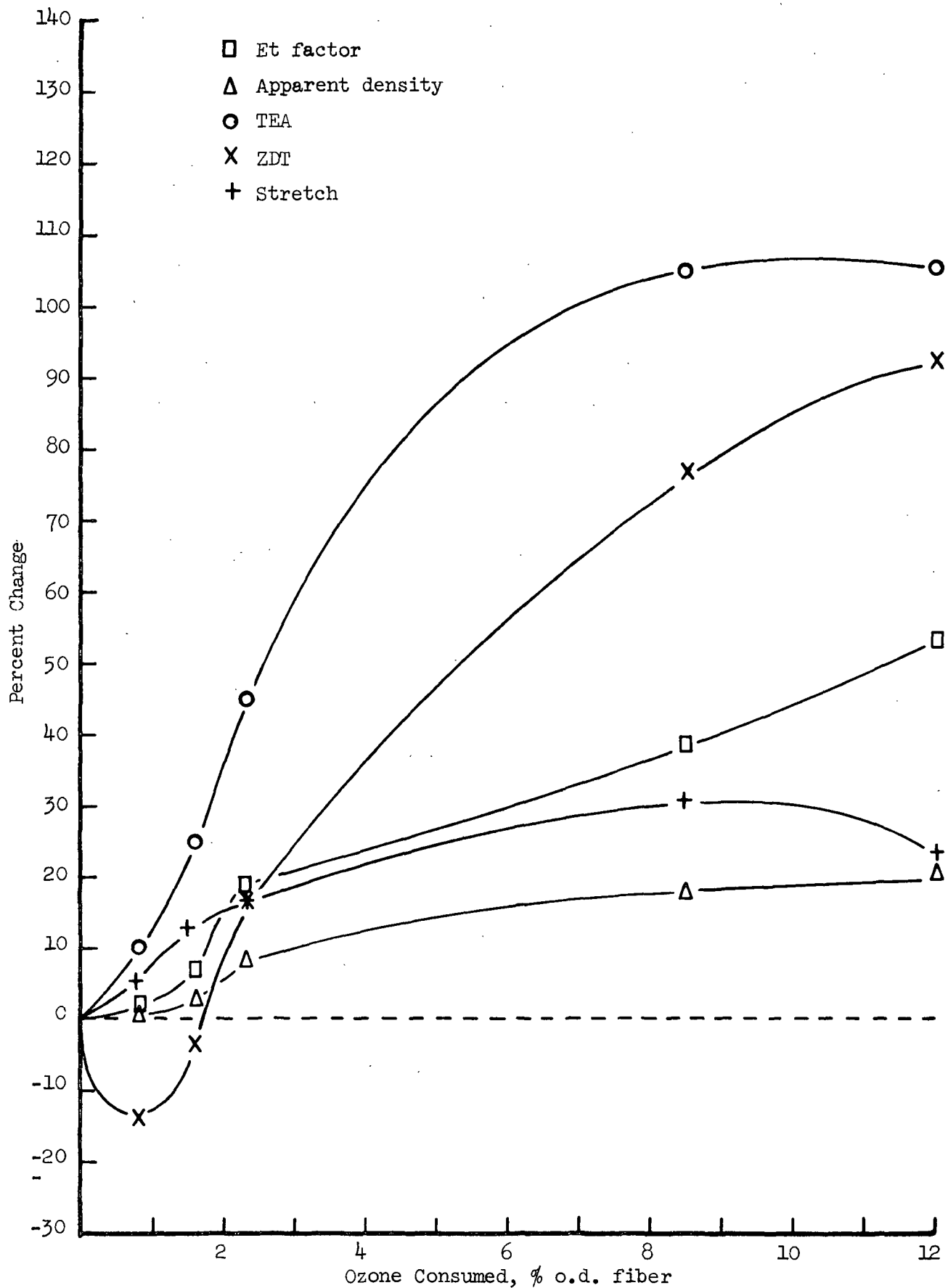


Figure 8. Effect of Ozonation on Handsheet Properties

which are highly dependent on fiber-to-fiber bonding. For example, at 2.3% O₃ consumption, the following percentage changes in properties were obtained:

Property	Percent Change at 2.3% O ₃
Freeness	-2.5
Apparent density	+8.3
Burst factor	+35.4
Tear factor	-2.9
Modified ring factor	+8.1
Tensile factor	+26.6
Stretch	+17.2
Tensile stiffness (Et) factor	+19.0
TEA	+45.0
Z-Direction tensile (ZDT)	+17.1
Brightness	+21.7
Zero-span tensile factor	-0.2

As may be noted, the burst factor increased +35.4%. The tensile factor increased +26.6%, and the other tensile load-elongation properties also exhibited large percentage improvements. The modified ring compression strength also increased but to a lesser extent (+8.1%). These improvements in properties were effected with only a small and probably not significant loss in freeness. Thus, the drainage resistance of the stock is not increased as would occur if the same effects were obtained by refining. In this sense ozonation appears to produce what might be termed chemical beating as noted by Proctor (18).

At the 2.3% O₃ level, a small loss (-2.9%) in tearing strength was obtained. Greater losses in tear were obtained at the higher ozonation consumption levels. Proctor (18) also obtained losses in tear on ozonation using kraft pulp.

In general, fiber strength, as measured by zero-span tensile, was not affected by the ozonation treatments. On the other hand, the Z-direction tensile

strength (ZDT) which is often used as a measure of bonding increased substantially at O_3 treatment levels of 2.3% and more. Thus, it appears that the improvements in such properties as burst are primarily due to increases in fiber-to-fiber bonding.

In general, lesser improvements in most physical properties were obtained at the 5 and 10 minute treatment times — ozone consumption levels of 0.81 and 1.59%, respectively. When the ozonated gas is first passed into the reaction flask, it must displace the air surrounding the fibers. The displacement must take some time — perhaps several minutes — during which time the fibers are probably not uniformly contacted by ozone. It appears likely that fibers near the ozone entrance tube have a greater opportunity to react than other fibers. Hence, the fibers may be nonuniformly treated in the initial stages under the reaction conditions employed. It may be speculated that a more uniform gas-solid contact in the initial reaction period might provide greater strength increases at shorter treatment times than were obtained.

The burst, tensile and freeness results are separately graphed in Fig. 9. The improvements in burst and tensile certainly appear to be significant at ozone treatments of about 2% or more, considering the variability between trials. Freeness decreased from about 635 to 617 cc at the 2.3% O_3 treatment which is probably not significant. Somewhat greater freeness decreases are obtained at the higher O_3 levels.

Figure 10 illustrates the effect of ozonation on various tensile load elongation characteristics. As mentioned, ozonation appears to significantly improve tensile stiffness (Et), the tensile energy absorption (TEA) and stretch. Increased tensile stiffness would be expected to increase the flexural stiffness

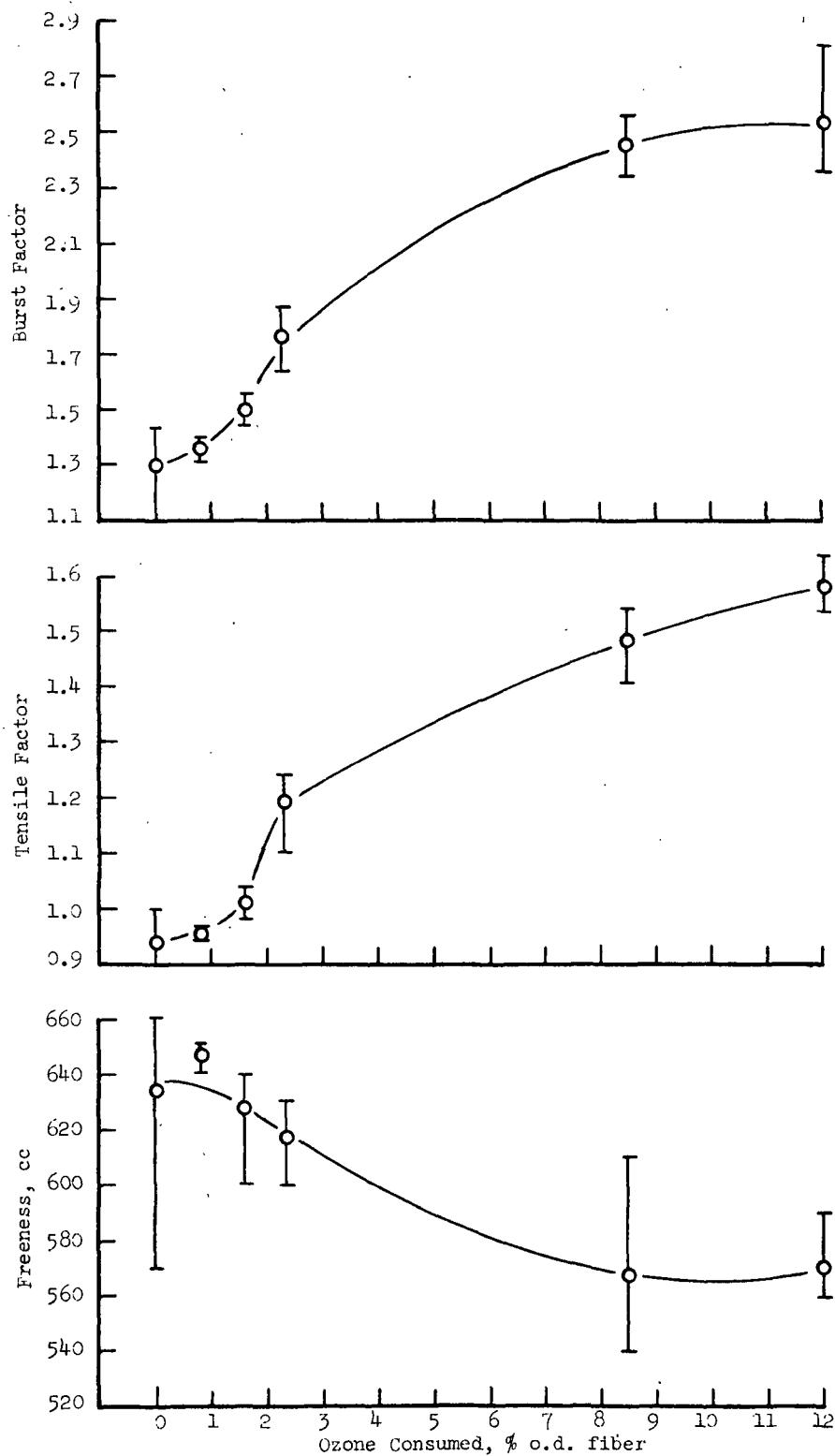


Figure 9. Effect of Ozonation on Burst, Tensile and Freeness
(brackets show maximum and minimum trial averages)

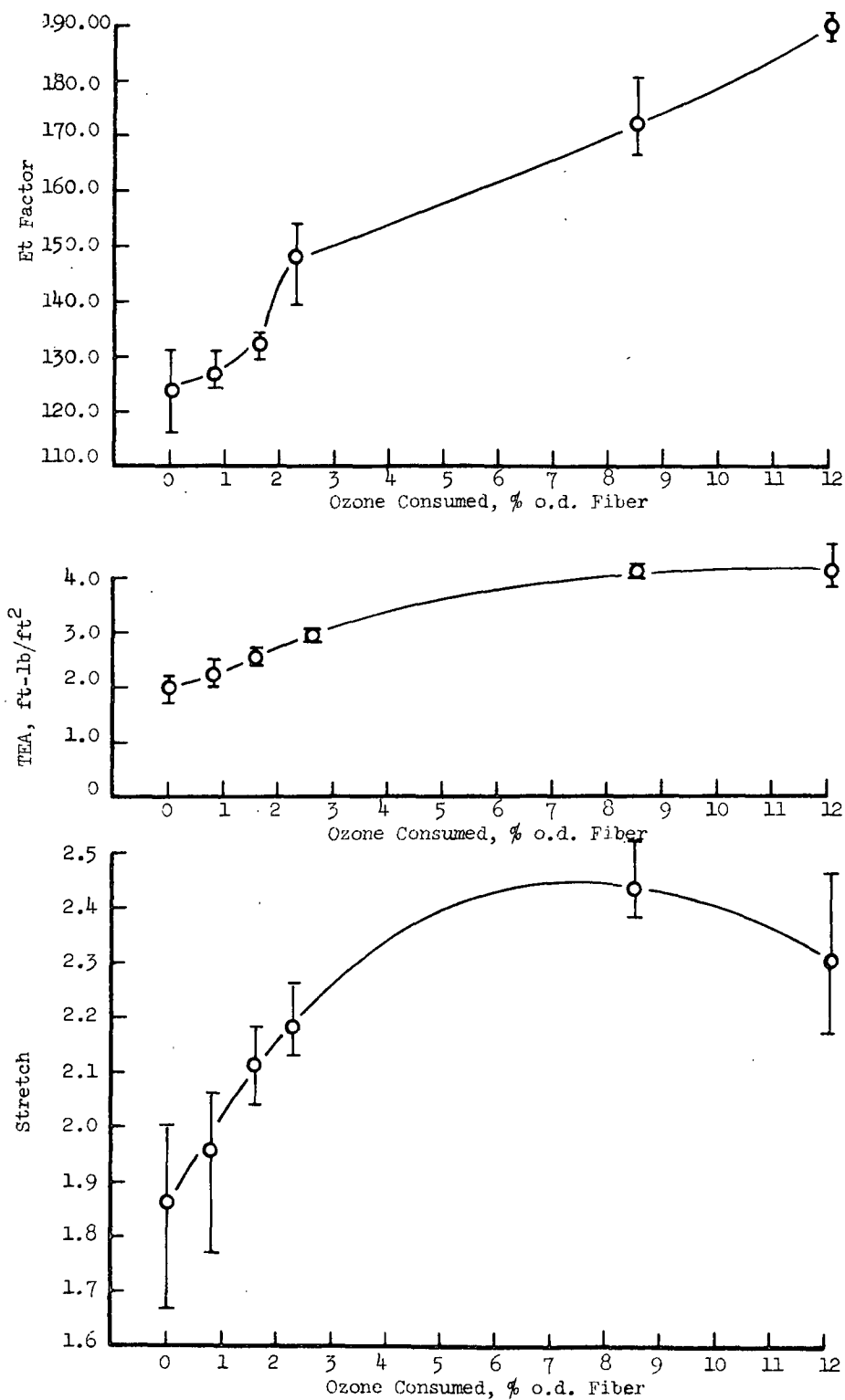


Figure 10. Effect of Ozonation on Tensile Stiffness (Et), TEA and Stretch (brackets show maximum and minimum trial averages)

of combined board and, hence, tend to increase box compression strength. Increased TEA may be of importance to other products where impact resistance is required.

The remaining physical properties are shown in Fig. 11 and 12. As mentioned previously, ozonation generally increased the average ring compression, density and ZDT bonding strength. The brightness of the sheets increased linearly with increased ozone consumption ranging from about 17% on the control to 45% at 12% O_3 treatment.

Briefly summarizing, it appears that:

1. Ozone treatments of OCC at levels of 2.3% or more significantly improve most strength properties. At ozone treatment levels of about 2.3%, little or no loss in freeness occurs. Thus, it should be possible to attain higher machine speeds for given strength levels.
2. The ozone treatments should present little or no effluent problem.
3. The ozone treatments should have no detrimental impact on the white water system such as may occur when polymers are employed.

In view of the above, further studies are underway on ozonation treatments as follows.

1. Process research.

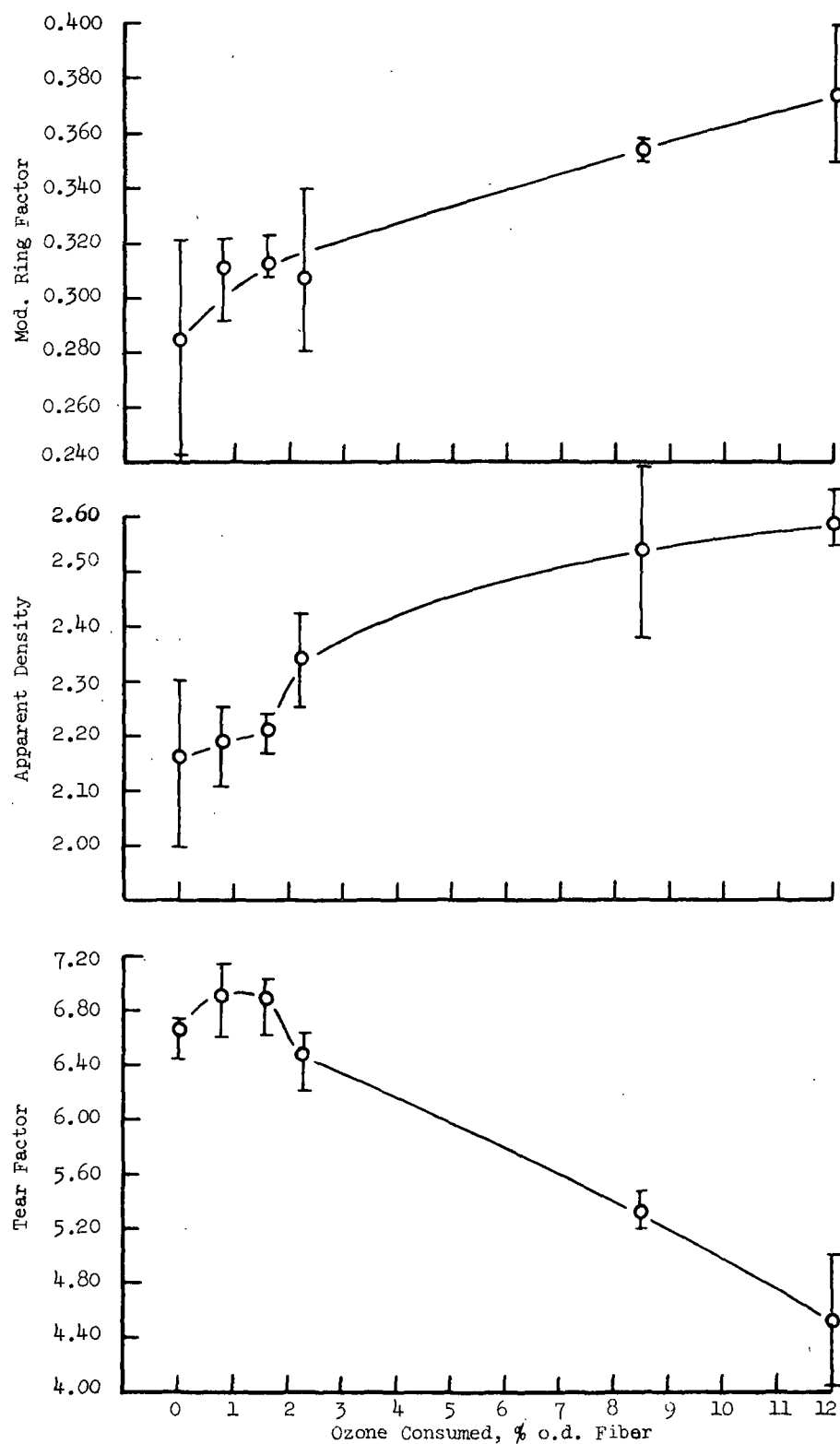


Figure 11. Effect of Ozonation on Ring Compression, Density and Tear Factor (brackets show maximum and minimum trial averages)

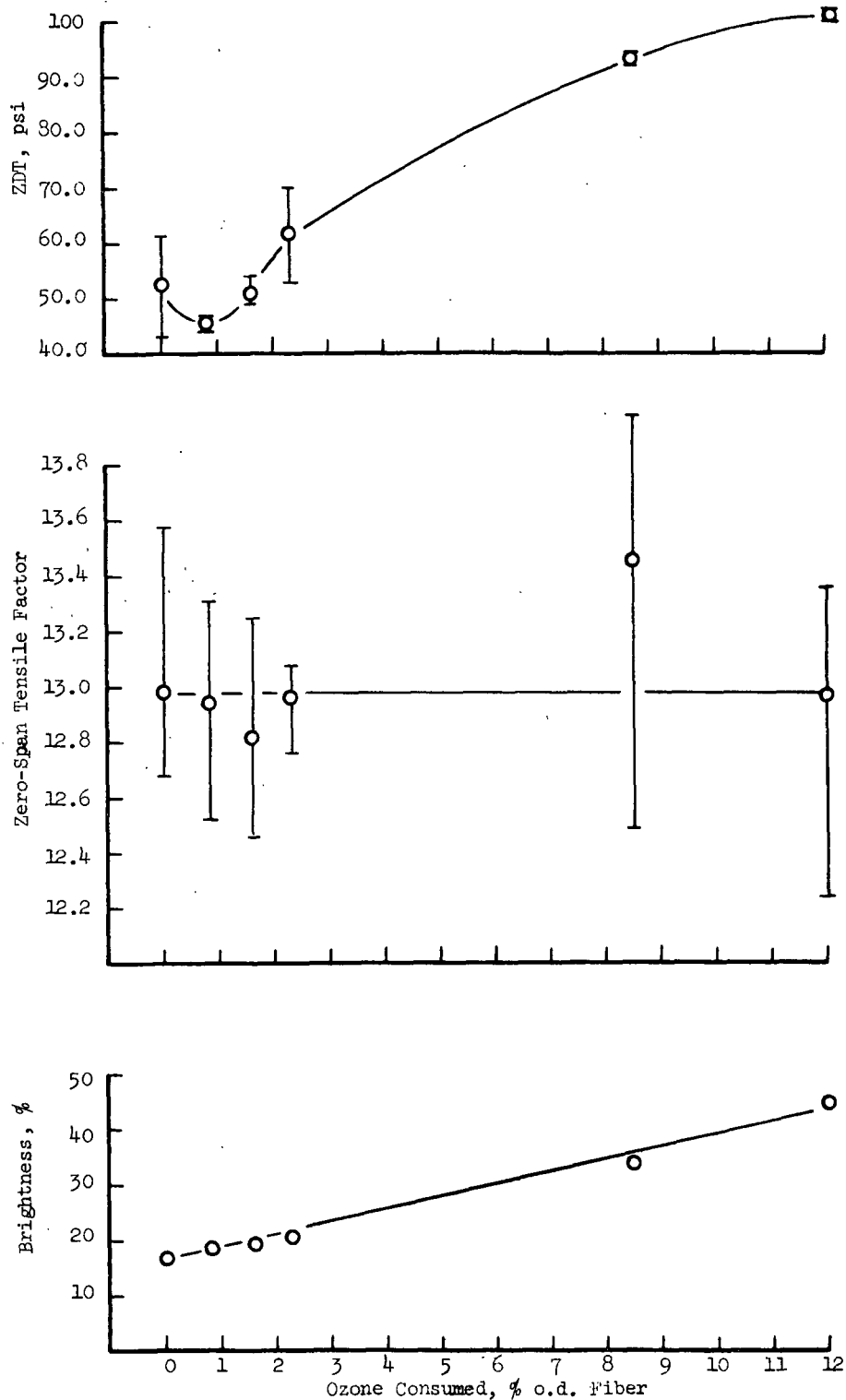


Figure 12. Effect of Ozonation on Z-direction Tensile (ZDT), Zero-span Tensile and Brightness (brackets show maximum and minimum trial averages)

2. Optimization of ozonated and untreated fiber combinations.
3. Pilot-scale process trials.
4. Process alternatives and costs.

PRELIMINARY PROCESS COST ESTIMATES

Preliminary estimates of the operating and capital costs which would be required in the ozonation process were obtained. The operating cost figures were obtained from a number of sources and were primarily based on the power required to produce ozone from O_2 . They include such additional expense items as maintenance and labor costs. The capital cost estimates are also subject to considerable uncertainty because of variables due to plant size, auxiliary equipment, etc. At this stage both the operating and capital cost items should be viewed as order of magnitude estimates. A list of companies supplying information on O_3 and O_2 generation is appended to this report.

The usual concentration of O_3 in O_2 is about 2%. It is believed that O_2 does not react with the pulp at the temperature (room temperature) and pressure employed. Thus, the O_2 effluent from the reactor can be recycled back to the ozone generator after being treated to remove other gases picked up in the reactor, e.g., water vapor, nitrogen, and any organic reaction gases. An O_2 recycling rate of 95% was assumed.

Reactor cost could be only crudely estimated at this time. It is speculated that a suitable reactor would be a vertical or inclined tubular vessel. The fluffed pulp would be fed by means of a screw feeder to the upper end, and the ozonated gas would be supplied to the other end and pass counter-current to the pulp.

The other main process steps involve dewatering to about 40-45% consistency and fluffing the pulp. Commercial equipment is available, and supplier estimates were used for the operating and capital costs. Uniform dewatering and fluffing to avoid overdrying and achieve a low bulk density in keeping with the reactor design may be quite important to treatment efficiency. Some study would be required to determine if present commercial equipment is satisfactory.

Tentative cost estimates to obtain a 35% burst improvement using 2.5% O_3 per o.d. ton are shown in Table VII. The capital estimates are arbitrarily based on a 300 tons/day plant treating OCC. The operating cost estimates varied from about \$12 to \$14 per ton apparently depending on supplier estimates of equipment requirements. It appears that a representative figure would be about \$12.50 per ton of treated fiber at a 2.5% O_3 treatment level — i.e., about \$5 per ton of fiber per percent O_3 addition.

The above estimates do not consider possible savings in refining energy. Because the ozonated fibers may require little or no refining, it appears that savings in refining energy could amount to \$1-\$4 per ton. This would reduce O_3 costs at the 2.5% treatment level from \$12.50 to about \$8.50-\$11.50 per ton. Capital costs are estimated to be about \$4.50-\$5.00 per ton of treated fiber based on a 10-year amortization period.

If a 35% burst improvement was achieved by increasing basis weight of commercial kraft linerboard using virgin kraft, it appears that an increase of 18 to 27 lb/M ft² would be required using average bursting strength results on commercial liner. This would correspond to a cost of \$43-\$64 per ton of linerboard.

TABLE VII
TENTATIVE COST ESTIMATES

Basis

35% Burst improvement, 2.5% O₃ applied per o.d. ton
300 tons/day OCC treated, 1000 tons/day linerboard production
O₃ Required: 7.5 tons
Power cost: 2¢/kw-hr
O₃ Concentration: 2% in O₂ or air
O₂ Recycling rate: 95%
Oxygen plant: 8 tons/day; 24-hr back-up supply

Costs (million \$)

Operational costs (annual)

O ₂ /O ₃ plant:	0.9-1.0
Fiber handling and reactor:	<u>0.4-0.5</u>
Operational totals	1.3-1.5

Capital	Equipment	Installation
O ₂ /O ₃ plant:	2.8-3.0	0.8-1.2
Fiber handling and reactor:	<u>1.0-1.2</u>	<u>0.2-0.4</u>
Capital totals	3.8-4.2	1.0-1.6

Costs per ton of treated fiber, %

Operation:	\$12.00-14.00
Capital (10-yr amortization):	<u>4.50- 5.00</u>
Total	\$16.50-19.50

Comparative virgin kraft cost (based on basis weight
change to improve burst 35% at a cost of
\$100/ton):

\$43-64

Thus, the initial cost estimates suggest that the ozonation process should have advantages in the treatment of pulp fibers to upgrade performance without sacrificing productivity.

The percentage changes in strength properties are graphed in Fig. 13 and 14 as a function of estimated ozonation processing cost. An "average" figure of \$5 per ton of fiber per % O_3 was used for plotting purposes, and it was assumed that O_3 addition levels of about 2.5% would be required as a minimum. In general, for a given cost, the greatest improvements are obtained in burst, tensile, tensile stiffness, and tensile energy absorption.

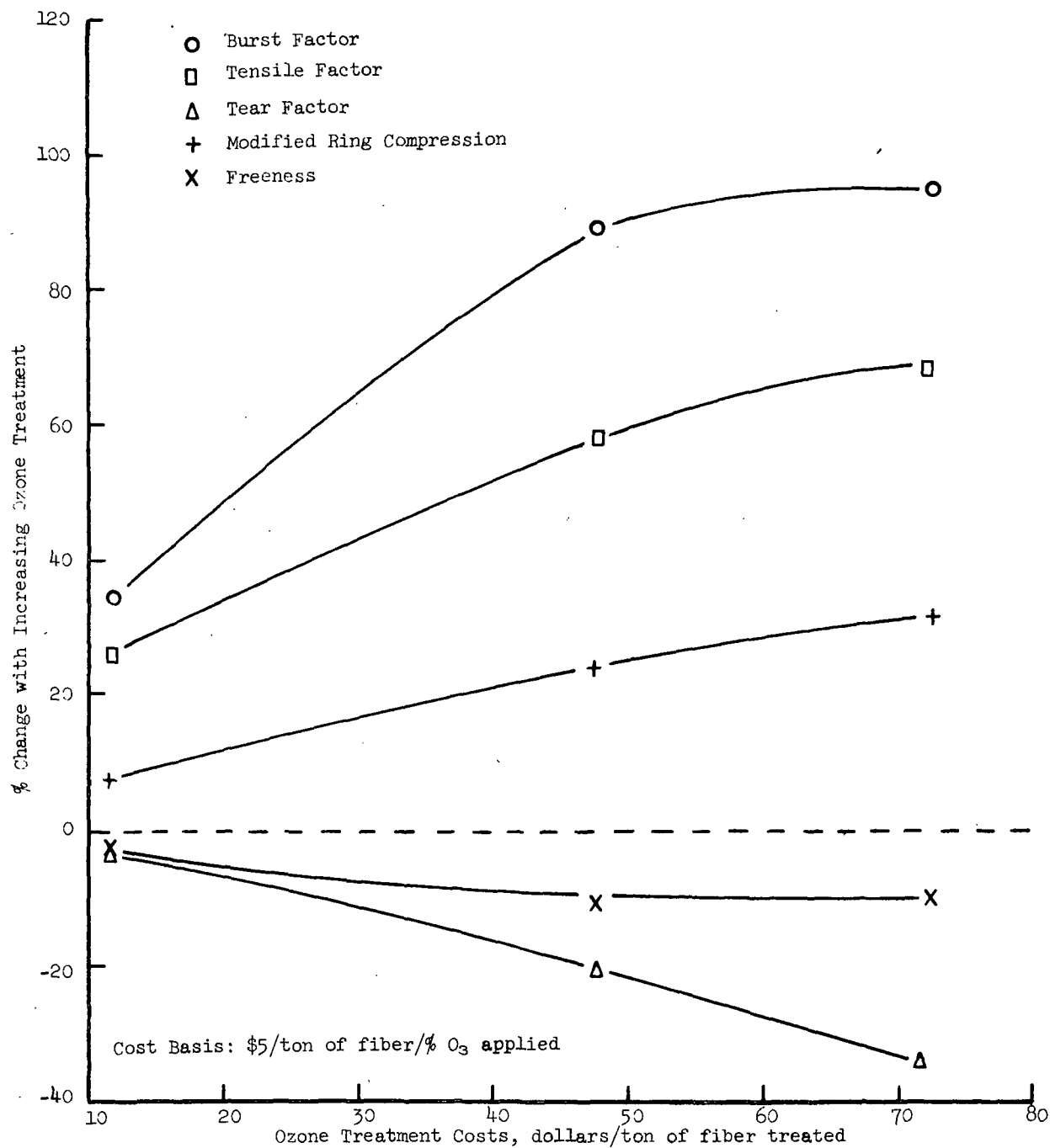


Figure 13. Change in Handsheet Properties vs. Ozonation Process Cost

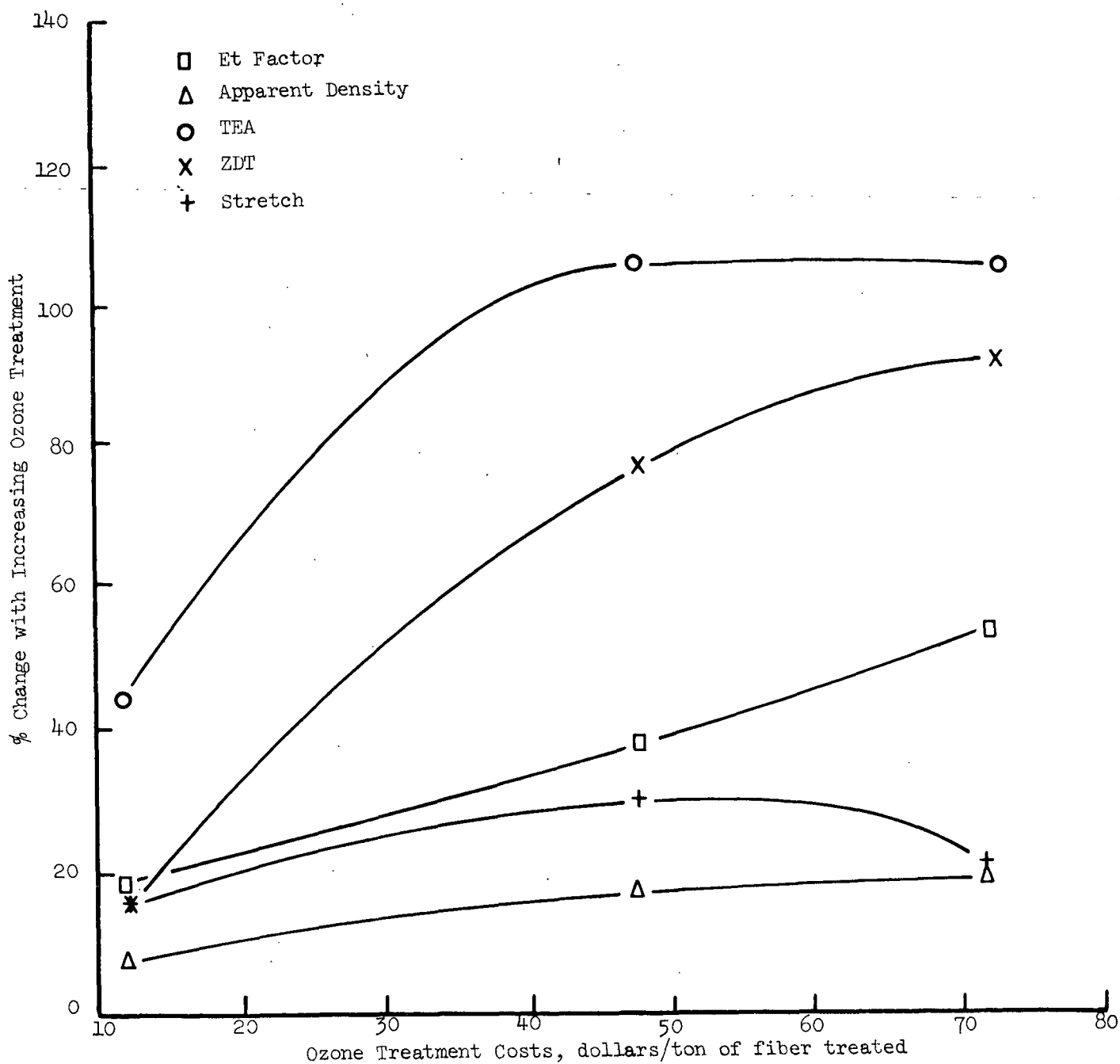


Figure 14. Change in Handsheet Properties vs. Ozonation Process Cost

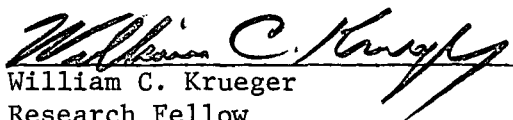
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Betty John
Research Fellow
Engineering Division

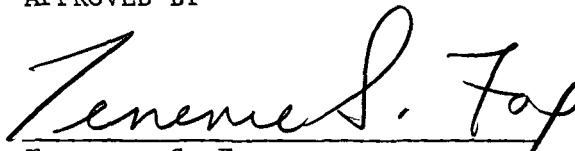


William C. Krueger
Research Fellow
Engineering Division



William J. Whitsitt
Research Associate
Engineering Division

APPROVED BY



Terrence S. Fox
Director
Engineering Division

APPENDIX I

COMPANIES SUPPLYING COST INFORMATION

Cochrane Environmental Systems
Crane Co.
800 3rd Avenue
P.O. Box 191
King of Prussia, Pennsylvania 19406

U.S. Ozonair Corp.
464 Cabot Road
South San Francisco, California 94080

Emery Industries
Ozone Technology Group
4900 Este Avenue
Cincinnati, Ohio 45232

Ingersol Rand
Pulp Machinery Division
150 Burke Street
Nashua, New Hampshire 03061

American Defibrator Inc.
7400 Metro Boulevard
Minneapolis, Minnesota 55433

Bepex Corp.
P.O. Box 880
Santa Rosa, California 95402

The Bauer Bros. Co.
Sub. of Combustion Engineering, Inc.
P.O. Box 968
Springfield, Ohio 45501

Chesapeake Corporation
West Point, Virginia

Air Products & Chemical Inc.
P.O. Box 538
Allentown, Pennsylvania 18105